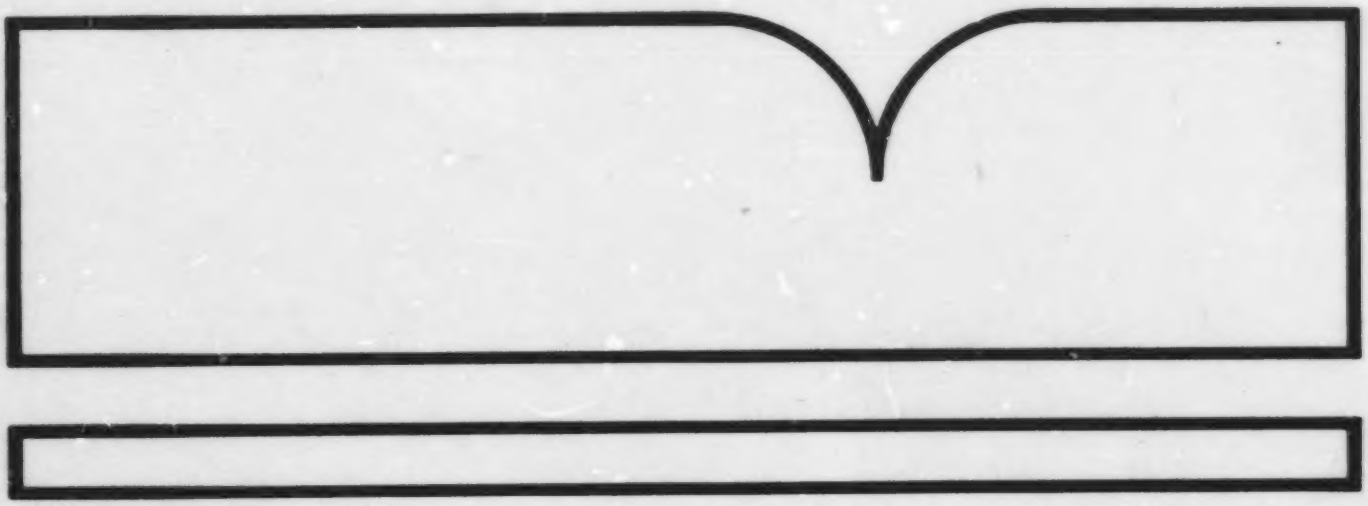
PB81-106890

Effects of Acid Precipitation

(U.S.) Corvallis Environmental Research Lab., OR

1979



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Norman R. Glass, Gary E. Glass, Peter J. Rennie

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1350

Effects of acid precipitation

Of what does it consist? What does it do to plant and animal life, water bodies, and other resources? Three experts explain

1351

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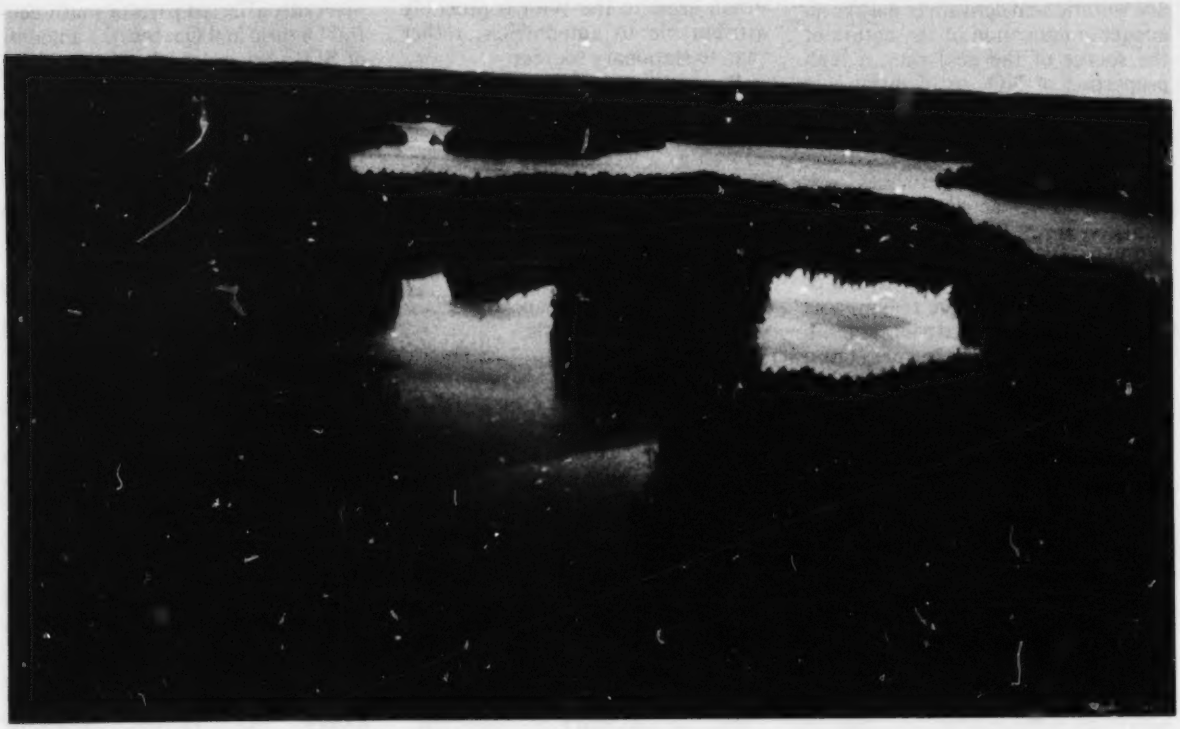
Although the historical record prior to 1955 on changes in acidity of precipitation is very sparse, there are data which indicate that by the mid-1950's, precipitation in the eastern U.S. was already acidic, and that the acidity of rain and snow in that region increased significantly between 1930 and 1950.



Vulnerable lake. *This one is in northern Minnesota*

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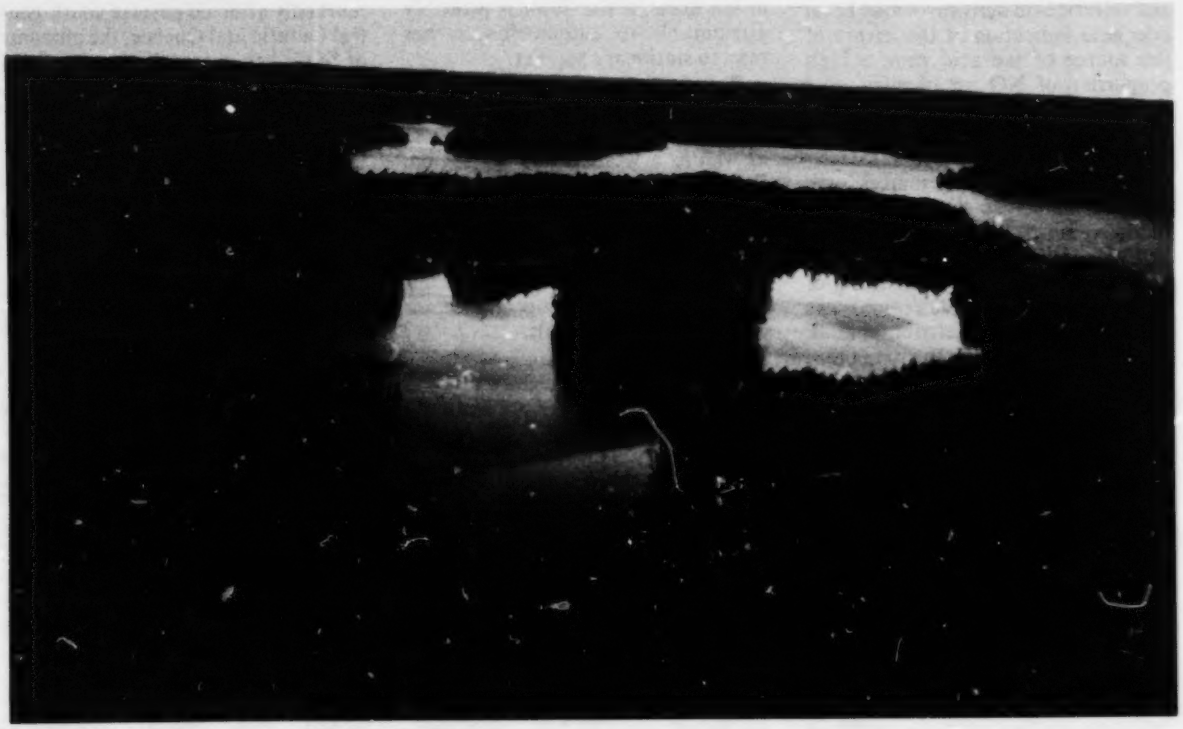

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A growing body of evidence suggests that acid rain is responsible for substantial adverse effects on the public welfare. Such effects include the acidification of lakes and rivers, with resultant damage to fish and other components of aquatic ecosystems; acidification and demineralization of soils; possible reductions in crop and forest productivity, and deterioration of manmade materials. These effects can be cumulative, or may result from peak acidity episodes.

A drop in the pH of precipitation has also been observed for many years in Scandinavia. A monitoring network there has shown that since the mid-1950's, precipitation in northwestern Europe has increased in acidity and is currently widespread, geographically. Indeed, the hydrogen ion concentration of precipitation in some parts of Scandinavia has increased more than 200fold during the past two decades.

The acids involved

Data from New York state and parts of New England indicate that approximately 60–70% of the acidity is ascribed to sulfuric acid, and 30–40% of the acidity to nitric acid. These strong acids are thought to stem primarily from gaseous manmade pollutants, such as sulfur oxides (SO_x) and nitrogen oxides (NO_x), produced primarily, although not exclusively, from the combustion of fossil fuels.

The relative proportion of nitric acid and sulfuric acid derivatives may be an adequate indication of the nature of the source of the acid rain; a high proportion of NO_x or of nitric acid derivatives suggest automobile or mobile sources. On the other hand, a high proportion of sulfuric acid derivatives indicate stationary sources, such as power plants, smelters, and heavy industry. It is interesting to note that in England, in the early part of this century, the acidity in the vicinity of Leeds (a heavy coal-use region) was approximately 75% attributable to sulfur compounds, and the pH in rain and fog appears to have dropped below 3.0 on occasion.

Emission sources for SO_x and NO_x are widely distributed within and outside urban centers. Contributions can come from both lower- and higher-height stacks, and from near-ground-level sources. Sulfates, including acid sulfates, are present in the stack gases associated with coal-fired and oil-fired sources.

The amounts of sulfuric acid and sulfates found in plumes can be sufficient to affect plume opacity and fallout of acid particles near the source. In plumes from elevated sources, lack of contact with the ground tends to preserve acid precursors for some distance downwind. Especially at night and in the early morning hours, ground-based inversions can isolate the plume aloft, so that near-source deposition is minimized.

The urban plume already contains organics, sulfur oxide, and nitrogen oxide precursors to sulfates and nitrates. Photochemical atmospheric reactions can form sulfates and nitrates relatively rapidly, as the urban plume progresses downwind. However, during periods of effective photochemical activity, urban plumes tend to be well mixed all the way to the ground. Therefore, dry deposition processes are competing with atmospheric reactions as sinks for SO_x and NO_x.

The most affected areas

At the present time, it is generally considered that, in this country, acid precipitation is most severe in the Northeast. However, recent data show the geographic extent of the problem to be increasing in the Southeast and Midwest, with all states east of the Mississippi affected to some degree. Furthermore, there is recent evidence of acid rain in the western U.S., at least in such major urban centers as the Los Angeles area, San Francisco, and Seattle. The ratio of sulfur derivatives to nitrogen derivatives (approximately 1:2) indicates that acidity in and near urban areas of the West is probably attributable to automobiles, rather than to stationary sources.

Precipitation analyses show that the acid rain problem extends into Canada, covering an extensive eastern area, as well as a western Alberta region. But regardless of where the problem is found, unlike more conventional atmospheric pollution, the pollution giving rise to acid rain may not exceed air quality standards, nor cause immediately obvious damage to receptor organisms and materials.

Emission tonnages

Emissions of SO_2 in Canada amount to around 6.5×10^6 metric tons annually. This gives rise to concern in three main areas, and several smaller ones. The major areas are the Sudbury region of Ontario (13 700 km^2), the Windsor-Sudbury-Montreal triangle in Ontario and Quebec (150 000 km^2), and the Grande Prairie-Edmonton-Pincher Creek triangle in southwestern Alberta (78 000 km^2). The isolated centers include Noranda and Murdochville, Quebec; and Thompson and Flin Flon, Manitoba.

In one of these major areas—Sudbury—high ambient concentrations of SO_2, acting with acid rain and particulates, have for many years been a major threat to vegetation and other environmental values. In the Windsor-Sudbury-Montreal triangle, local emissions have not by themselves generated problems, but steady urban-industrial expansion, combined with large emissions in surrounding areas, have had effects exceeding the normal resilience of environmental characteristics, particularly that of water bodies. By comparison, emissions in southwestern Alberta from sour-gas processing do not yet constitute a serious threat, but certain of the region's agricultural crops are highly sensitive.

The comparable tonnage for the U.S. is approximately 3.8×10^8 metric tons/yr. However, emission rates from the U.S., as compared to Canadian sources, do not necessarily indicate net transboundary flux or deposition rates. Major source regions of the U.S. include the Ohio and Tennessee Valleys, the North Central and Northeast industrial areas, and the Washington, D.C., to Boston urbanized corridor.

Data from the Canadian precipitation sampling and analysis network (CANSAP) show that large parts of eastern Ontario, stretching from the Manitoba-Ontario border to Newfoundland, are receiving substantial amounts of SO_4^{-2} in the form of wet deposition. Moreover, in the more markedly affected parts of south-central Ontario and Quebec, the amounts of SO_4^{-2} being deposited range from 18–78 grams of SO_4^{-2}/ha/y. Such deposition rates are somewhat less than those being received in the more severely affected parts of the northeastern U.S., but they are of the same general order as those recorded in Scandinavia, where serious environmental damage has occurred.

Impacted materials

Serious though these emission and deposition data appear, it must be recognized that they can begin to take on a degree of significance only when the nature and properties of the impacted materials are also taken into account. For this reason, precipitation would have to become very acid, indeed, in the Canadian Prairies to generate environmental concern for calcareous, or sulfur-deficient soils. The same holds for the calcareous and neutral soils of southern Ontario, in spite of appreciable sulfate loadings. However, for most of eastern Canada, soils are podzolic, and not well endowed with nutrient elements, displaying natural acidities ranging

from about pH 4 in the surface horizons to around 5.5 in the lower parts of the profile.

In general, then, the picture for much of eastern Canada is that of a bedrock geology with surficial deposits giving rise to acidic soils and water bodies that are naturally low in alkalinity and calcium reserves. Their neutralizing ability is limited, and their resistance to further acidification is severely tested when the strongly dissociated sulfuric acid, brought in by acid rain, supplants a system normally stabilized by the far less strongly dissociated association of carbonic, and other organic acids.

However, such terrestrial and aquatic systems must not be thought of as being unproductive and of little ecological or economic significance. For the forest resource alone, for example, in eastern Canada, the direct value (after processing) is on the order of $4 billion/yr. Indirect and intangible values in providing recreation, maintaining habitats for wildlife, stabilizing river flow, preventing soil erosion and the siltation of water bodies, and aesthetic appearances are all inestimable. Forest growth rates are not as high as in other more favored soil and climatic zones of North America, but this merely means that larger areas have to be more soundly managed in eastern Canada, than elsewhere.

As the U.S. places increasing reliance on coal as an energy source because of crude oil prices and foreign crude oil supply problems, as well as public questions about the safety of nuclear power, air emissions from energy producers will increase. Thus, switching fuel from natural gas or oil to coal will make the task of reducing sulfur emissions from new and existing power plants difficult. Mobile and stationary sources of NO_x will also continue to contribute to the overall loading of acidity to the aquatic and terrestrial environment. In brief, it seems probable that acid deposition to the environment will at least remain at present levels, and might be expected to increase over the next decade or two.

Lake sensitivity

As more coal-fired power plants are built and become operational, especially upwind of the west-central U.S., and in the Midwest and Southeast, the capacity of affected watersheds to neutralize the atmospherically-deposited acids will be exhausted. The point at which significant change in the pH of lakes occurs may be called the "threshold" of lake acidification. This threshold value for Swedish lakes has been determined as that point at which the atmospheric loading of acid has caused the annual average pH of precipitation to be depressed to pH 4.6 or below. Increased acid loading beyond the threshold value has resulted in more than 15 000 fishless lakes in Sweden.

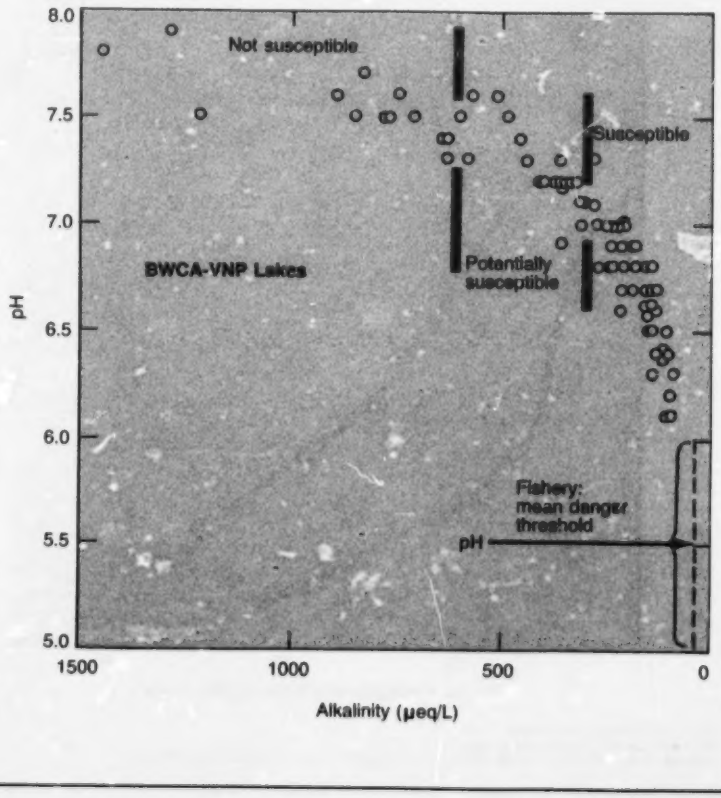
The transferability of this threshold value to U.S. watersheds (lakes) will depend on the similarity of the environmental factors of the watersheds, and primarily on the lack of acid-neutralizing (or alkaline) soils. This single primary factor defines the geographic regions which are extremely susceptible to acid precipitation. Lakes in the Adirondack State Park of New York and the Boundary Waters Canoe Area—Voyageurs National Park (BWCA-VNP) of Minnesota are examples of such susceptible environments in the U.S.

In the Adirondack area, the threshold acid precipitation value has been exceeded for several years. As a result, lake pH values are depressed to the point at which fish have stopped reproducing, and more than 100 lakes are now fishless. Portions of eastern Canada have similarly been receiving acid deposition which has exceeded the threshold value for lake acidification.

In the BWCA-VNP, the process of lake acidification is just beginning, and only the most susceptible lakes are being affected. This area is one that exhibits the properties of maximum sensitivity to acidification because of extremely soft waters, thin soils, and very sensitive terrestrial and aquatic plants and animals. In addition, the BWCA is a wilderness area which the U.S. Congress has taken extreme care to preserve against the impacts of "development" (P.L. 95-495) to the that *no* man-induced changes are desired. As a wilderness area, it is also a Class I air quality maintenance area under the Clean Air Act of 1977.

Like the Adirondack Park area, the BWCA-VNP region rests on acidic bedrock, and thus meets the main criterion for an acid-sensitive classification. Of the midwestern states, only upper Michigan, northern Wisconsin, and northern Minnesota have this type of bedrock covering wide areas. The lakes in the BWCA-VNP area have been surveyed only recently for possible impacts from acid precipitation; the results are shown in Figure 1.

FIGURE 1
pH/alkalinity relationship



About two-thirds of the 85 lakes sampled in 1978 and 1979 are susceptible to change from acid precipitation. If these lakes are representative of the 1500 lakes in the BWCA-VNP, then the potential for severe ecological damage is serious. The annual average pH of precipitation in this region is just at the edge of 4.6. Contributions from increasing emissions, including six major coal-fired power plants, being built or just completed in the area, will certainly increase the rate of acidification.

Sulfate loadings

Another measure of the acidification process is shown in Figure 2. Since a major source of acid in precipitation is related to sulfur emissions, the extent of lake acidification has been measured as a function of annual atmospheric loadings of sulfate for lakes in southern Sweden. The sharp drop of this pH curve for extremely sensitive lakes shows how a slow increase in "added increments" can and will cause a sharp break in the response curve. This response is characteristic of very-soft-water lakes in which only a small amount of bicarbonate is available to neutralize the incoming acid. The pH remains relatively constant until all of the carbonate is consumed; then the stronger organic and sulfuric acids control the lake pH. In other words, the assimilative capacity (or buffer capacity) of the lake has been exhausted, as indicated by the break point and downward slope, especially on curve 1 of Figure 2.

The general shape of the sulfate loading-pH response curve shown in Figure 2 is also expected for an individual lake as the acid loading from atmospheric sources is increased over time. For a given region where the loading is fairly constant, the pH response of lakes may be described as a series of response curves, similar to those in Figure 2, each reflecting individual differences and characteristics of the particular lake watershed.

Some of the factors which control the shape and displacement of these loading-pH responses are watershed area–lake/volume ratio, soil-geology factors, vegetative cover, groundwater input, organic acid input from bogs, displacement of toxic metals such as aluminum and manganese, and a host of other factors yet to be defined. The size of watershed and stream order have also recently been discussed as factors in pH loading. If the acid loading to a particular region is limited to the amounts defined by the upper portions of the response curves for sensitive lake systems, then the magnitude of the damage to the aquatic environment can be minimized.

Unamended soils and forests

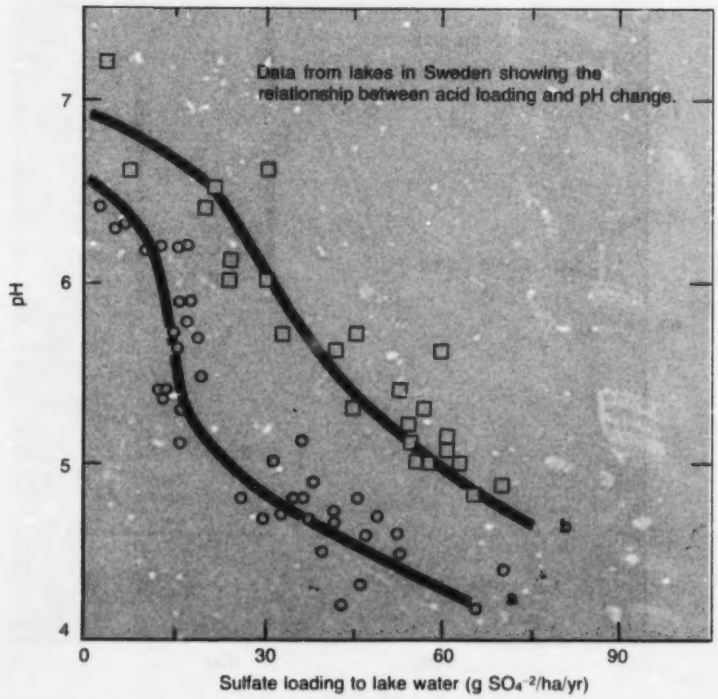
Beginning in the 1930's, the federal Canadian Forestry Service has been involved in terrestrial research on air pollution effects for many years, dealing with problems at Trail, British Columbia, and with the separation of pollution effects on forests from effects attributable to insect and disease attack. Since that time, there have been numerous signal contributions to the understanding of pollution problems, usually from data taken near strong point emitters.

In perspective, although there may seem to be many features common to the problems of acid rain and of other atmospheric pollution, regardless of how they originate, there are two important differences. First, pollution over a long range of time and distance usually does not exceed conventional air quality standards. Second, it may not cause any spectacular or immediately measurable reduction in tree growth. Therefore, a superficial view, or one based on a ranking in priority of more obvious disasters, would fail to discern much of a problem.

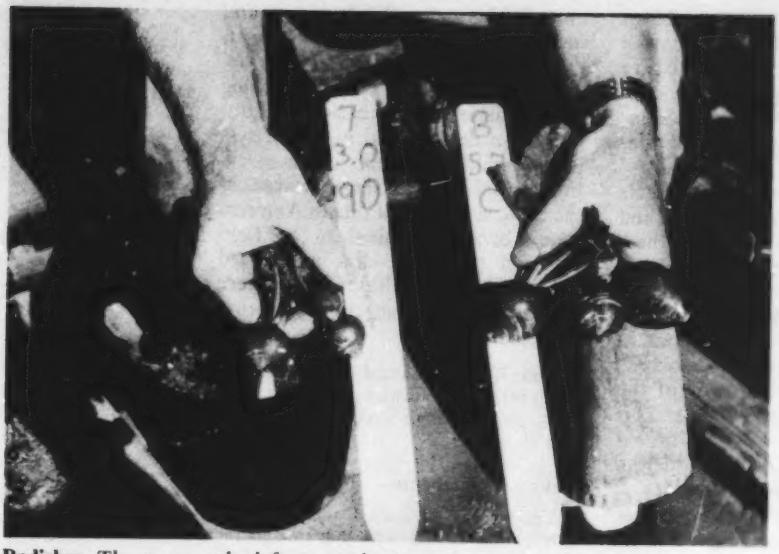
Early research may now seem very far in the past, but it resulted in a striking demonstration of soil acidification and calcium removal, and aluminum solubilization effects as a consequence of repeated sulfate fertilizer applications are well-documented. Indeed, it was shown that acid rain could ultimately result in permanent reduction in tree growth and site quality. Useful soil microorganisms would be eliminated, and potentially toxic soil elements, such as aluminum and manganese, brought into solution to exercise deleterious effects on plant roots and nutrient absorption. Moreover, since heavy metal particulates sometimes accompany gaseous pollutants, a situation could arise in which such noxious elements are held preferentially on the exchange sites of colloids, at the expense of the more useful monovalent and divalent cations.

Unlike the situation in aquatic systems, however, there seems to be a more acidic state of podzolic forest soils, so that acid rain may not very readily lower the pH further, or induce further losses in bases. However, the complex makeup of soils prevents the pinpointing of a sharply critical soil pH

FIGURE 2
Sulfate loading effects in lakes



[a]For very sensitive lake systems
[b]For somewhat less sensitive lake systems
Source: William Dickson, National Swedish Environmental Protection Board (Jolna, Sweden)



Radishes. *The ones on the left are acid rain victims; pH was 3 for the experiment at EPA*

Model. *Forest ecosystem simulation at EPA, Corvallis, for acid rain studies*

value separating adverse and nonadverse effects of acid rain. Nevertheless, it seems likely that the approximate value lies within the pH 4.0–5.5 gradient, such as that seen in eastern Canada podzol profiles.

New approaches to defining critical pH values, not based on strong point emitters, include "sensitivity mapping". They can be very crude—such as the separation of areas of calcareous and noncalcareous bedrock, or the identification of sulfur deficient soils—or they may be more finely-tuned, and based on a synthesis of soil attributes. Considerable progress has been made in grading the sensitivity of Ontario lakes, using alkalinity as an index, and it is possible that a somewhat similar index, based on exchangeable calcium status, could be used for soils. For at least the reasons that are explained above, however, such a soil sensitivity index may always be no more than a very crude indicator.

Of particular value are lysimetric-type studies in progress. Representative monoliths are being percolated, with known amounts of simulated rain, to test the rate at which horizons change their properties as well as the speed of calcium release. Knowing the sulfate loadings that such soils are sustaining under natural conditions, one can gather that the results from such lysimetric installations should permit approximate predictions of soil changes under field conditions.

Agricultural effects

There are two basic ways acidic precipitation could have an impact on agricultural crops. First, acidic precipitation can directly affect the foliar surface of the plant itself, thus acting on the leaf or stem of the crop plant. In these cases, the most immediate effect would be on crops such as lettuce, spinach, or chard, of which the foliage is the valuable portion. Second, acidic precipitation can indirectly affect the crop plant through effects on the soil. For example, changing the pH of rainfall which strikes the soil can change the rate at which nutrients are recycled; the speed with which litter and other organic materials are broken down through microbial action in the soil; and the rate at which both macronutrients and micronutrients are leached from the soil into surface waters, or into ground waters. Detailed physiological mechanisms whereby these two basic impacts are manifest have been discussed elsewhere.

At a pH below 3.0, areas of leaf surfaces have generally been observed to become spotted or necrotic. For obvious reasons, vegetables, as well as ornamental plants may be unmarketable after exposure to rain or mist at or near pH 3. It should also be clear that with decreases in functioning leaf area, the photosynthetic process itself must be decreased, and the productivity of the plant must necessarily decrease.

With changes in aboveground biomass such as would be experienced under low pH rain, belowground biomass would be similarly decreased. It is not yet known what the relationship is between percent of leaf area affected (non-functional due to necrotic areas), and percent change in growth for plants. However, it is known that with depressed pH, foliar losses of important nutrients such as K^+, Mg^{++}, and Ca^{++} are observed. Also, nutrient cycling changes in either agricultural land or forestry land can result in lowered fertility over the long term, as well as decreases in essential soil nutrients which are required for normal plant growth.

It has been determined that in three out of five host-parasite systems involving oak trees and kidney beans, alterations occurred in the pathogenicity of the parasite under conditions of artificial sulfuric acid precipitation at pH 3.2. An additional observation was that the root nodule number and the nitrogen fixation of kidney beans were diminished by sulfuric acid rain at pH 3.2, and that bean yield was decreased in low cation exchange capacity soils but not decreased in higher cation exchange capacity (greater than 3 meq/100 g soil) soils.

Rainwater at approximately pH 4.0, whose low pH is caused by volcanic activity in the Kona district of Hawaii, is known to affect tomatoes adversely. While 5 kg per plant of salable fruit were obtained from tomato plants grown under a plastic rain shelter, no salable fruit was produced on plants growing immediately outside the rain shelter.

While it is possible that gaseous pollutants, such as SO_2, may also be present near fumaroles or volcanic activity, the fact that the plastic rain shelter had no sides, but still provided enough protection to the plants to permit fruiting, indicates that gases alone are probably not the cause. It is possible that the causative agent was not rainfall, but dry fallout. This possibility should be investigated experi-

mentally. However, it has been shown that cations, plant-growth-regulating substances, and other materials are leached from growing plants by acid rainfall, and that leaching rates increase for many materials as pH decreases.

While the data relating the effects of acid precipitation on crop yield and production are somewhat sparse, there is every indication that acid rainfall is deleterious. In order to pursue this hypothesis somewhat further, an extensive screening program to look at the effect of sulfuric acid rain on virtually every major field crop of the U.S. has been initiated by EPA. This study has been undertaken at an experimental farm facility in order to determine the sensitivity of crops to simulated acid precipitation because of the potential for widespread economic damage to a number of field crops. Final results from this study are expected by the summer of 1980. Preliminary indications of effects of simulated acid rain on yields of certain early-maturing crop varieties, such as peas and broccoli, are expected by fall, 1979.

A concerted attack

In summary, there is substantial reason to suspect that the deposition of acidic precipitation, especially in wide geographic areas of the eastern U.S. and Canada, will have adverse effects on aquatic systems, forests, and agricultural systems. The latest evidence suggests several avenues of research which should be pursued to define further the magnitude and extent of the effects of acid precipitation on resources.

The cumulative threat of acid precipitation is recognized, and a concerted attack is being spearheaded by Environment Canada and the U.S. Environmental Protection Agency (EPA) that brings together different disciplines and jurisdictions. Ongoing pollution studies, based on strong point emitters, and special new investigations are being applied in a number of promising approaches. These include the use of sensitive lichens as indicator species, pre-visual biochemical tests on tree and other plant tissues, differential depositional patterns of pollutants on soils, and delineation of "sensitive" soils, forests and water bodies.

While direct effects on terrestrial and aquatic ecosystems should be investigated intensively, indirect effects on the abiotic components of such systems should also be studied. For instance, a number of processes involving the impact of acidic precipitation on soil systems, including both amended agricultural soils and natural forest soil systems, need to be investigated. Processes such as soil litter decomposition, nutrient cycling, leaching of nutrients and other cations and anions from natural and managed systems should be objects of research. Further definition of sensitive areas of the eastern portion of North America should be accomplished, so that field research programs can be focused geographically in those areas where the impact is suspected of being greatest.

Note: References and documentation are available from Norman R. Glass, U.S. EPA, 200 S.W. 35th Street, Corvallis, Ore. 97330

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Gary Glass (*l.*) *is the senior research chemist at the U.S. EPA Environmental Research Laboratory-Duluth and is responsible for identifying and defining developing environmental problems. Dr. Glass is currently studying methods to determine pollutant chemical speciation in the environmental and regional impacts of coal-fired power plants on sensitive ecosystems.*

Peter Rennie (*r.*) *is an environmental analyst with the Policy Development and Analysis Branch of the Canadian Forestry Service. As a physical scientist specializing in biological problems, Dr. Rennie has been much concerned with forest soils, mineral nutrition and cycling, and the impact of pollutants and industrial developments.*